Effect of rapid high-intensity light-curing on polymerization shrinkage properties of conventional and bulk-fill composites

Par, Matej ; Marovic, Danijela ; Attin, Thomas ; Tarle, Zrinka ; Tauböck, Tobias T

Abstract: OBJECTIVES To compare the effect of high-intensity (3 s with 3440 mW/cm^2) and conventional (10 s with 1340 mW/cm^2) light-curing on shrinkage properties and degree of conversion of conventional and bulk-fill resin composites, including two composites specifically designed for high-intensity curing. METHODS Real-time linear shrinkage and shrinkage force of 1.5 mm thick composite specimens were measured for 15 min after the start of light-curing using custom-made devices. From the shrinkage force data, maximum shrinkage force rate and time to achieve maximum shrinkage force rate were determined. Degree of conversion was measured using Fourier transform infrared spectrometry. RESULTS Flowable composites showed significantly higher linear shrinkage compared to sculptable composites (1.93-2.91 % vs. 1.15-1.54 %), as well as significantly higher shrinkage forces (18.7-24.4 N vs. 13.5-17.0 N). Degree of conversion amounted to 45.8-60.1 %. For high-intensity curing, degree of conversion was significantly lower in three out of seven composites, whereas shrinkage forces were either increased, decreased, or unchanged compared to conventional curing. For high-intensity curing, maximum shrinkage rates were 6-61 % higher, whereas times to achieve maximum shrinkage force rate were 15-53 % shorter compared to conventional curing. Composites specifically designed for high-intensity curing showed shrinkage parameters comparable to other investigated composites. CONCLUSION Shrinkage behavior under conditions of high-intensity light-curing was material-dependent. Shrinkage force kinetics were more strongly affected by high-intensity curing than absolute values of linear shrinkage and shrinkage force. CLINICAL SIGNIFICANCE Despite being attractive for its convenience, high-intensity curing can lead to considerably faster development of shrinkage forces in the early stage of polymerization.

DOI: https://doi.org/10.1016/j.jdent.2020.103448

DOI: https://doi.org/10.1016/j.jdent.2020.103448

Journal of Dentistry 101 (2020) 103448

Contents lists available at ScienceDirect

Journal of Dentistry

journal homepage: www.elsevier.com/locate/jdent

Effect of rapid high-intensity light-curing on polymerization shrinkage properties of conventional and bulk-fill composites

Matej Par [a,b,*], Danijela Marovic [b], Thomas Attin [a], Zrinka Tarle [b], Tobias T. Tauböck [a]

[a] Department of Conservative and Preventive Dentistry, Center for Dental Medicine, University of Zurich, Plattenstrasse 11, Zurich, Switzerland
[b] Department of Endodontics and Restorative Dentistry, School of Dental Medicine, University of Zagreb, Gunduliceva 5, Zagreb, Croatia

ARTICLE INFO

Keywords:
Bulk-fill composite
Ultra-fast light-curing
Polymerization contraction
Polymerization shrinkage stress
Degree of conversion

ABSTRACT

Objectives: To compare the effect of high-intensity (3 s with 3440 mW/cm^2) and conventional (10 s with 1340 mW/cm^2) light-curing on shrinkage properties and degree of conversion of conventional and bulk-fill resin composites, including two composites specifically designed for high-intensity curing.
Methods: Real-time linear shrinkage and shrinkage force of 1.5 mm thick composite specimens were measured for 15 min after the start of light-curing using custom-made devices. From the shrinkage force data, maximum shrinkage force rate and time to achieve maximum shrinkage force rate were determined. Degree of conversion was measured using Fourier transform infrared spectrometry.
Results: Flowable composites showed significantly higher linear shrinkage compared to sculptable composites (1.93–2.91 % vs. 1.15–1.54 %), as well as significantly higher shrinkage forces (18.7–24.4 N vs. 13.5–17.0 N). Degree of conversion amounted to 45.8–60.1 %. For high-intensity curing, degree of conversion was significantly lower in three out of seven composites, whereas shrinkage forces were either increased, decreased, or unchanged compared to conventional curing. For high-intensity curing, maximum shrinkage rates were 6–61 % higher, whereas times to achieve maximum shrinkage force rate were 15–53 % shorter compared to conventional curing. Composites specifically designed for high-intensity curing showed shrinkage parameters comparable to other investigated composites.
Conclusion: Shrinkage behavior under conditions of high-intensity light-curing was material-dependent. Shrinkage force kinetics were more strongly affected by high-intensity curing than absolute values of linear shrinkage and shrinkage force.
Clinical significance: Despite being attractive for its convenience, high-intensity curing can lead to considerably faster development of shrinkage forces in the early stage of polymerization.

1. Introduction

Since the inception of resin composites as dental restorative materials, polymerization shrinkage and the associated stress have been persistent issues [1]. Polymerization shrinkage stress exerts a detrimental effect on marginal integrity [2] and may be related to post-operative sensitivity, enamel cracking, marginal staining, and eventually secondary caries [3]. Recognizing shrinkage stress as a significant disadvantage of all resin composites, various solutions for its reduction have been investigated, including adjustments of material compositions and changes in light-curing protocols [4]. Modified light-curing protocols that involved prolonging the initial polymerization phase (e.g. soft-start and pulse-delay protocols) were based on an assumption that slower curing would allow more viscous flow before the majority of shrinkage stress starts to build up [5]. Inconsistent evidence for the benefits of these modified protocols for reducing shrinkage stress stems from the fact that a slower polymerization does not necessarily delay the development of composite's elastic modulus [6]. As the soft-start and pulse-delay polymerization protocols did not fulfill the expectations of mitigating shrinkage stress to a clinically useful extent [3,7], protocols employing high-intensity light and short curing times became attractive as part of the general trend of simplification of

* Corresponding author at: Department of Conservative and Preventive Dentistry, Center for Dental Medicine, University of Zurich, Plattenstrasse 11, Zurich, Switzerland.
E-mail addresses: mpar@sfzg.hr (M. Par), marovic@sfzg.hr (D. Marovic), thomas.attin@zzm.uzh.ch (T. Attin), tarle@sfzg.hr (Z. Tarle), tobias.tauboeck@zzm.uzh.ch (T.T. Tauböck).

https://doi.org/10.1016/j.jdent.2020.103448
Received 7 April 2020; Received in revised form 12 July 2020; Accepted 4 August 2020
Available online 7 August 2020

restorative procedures [8]. This led to radiant exitances of about 1000 mW/cm^2 becoming standard for light-curing of contemporary composites [9].

The overall trend of simplifying restorative procedures has continued with the recent introduction of two bulk-fill resin composites, which are specifically designed for rapid high-intensity light-curing [10]. When used with the corresponding curing unit featuring a nominal radiant exitance of 3000 mW/cm^2, these materials are advertised as suitable for being light-cured in 4 mm thick layers within 3 s. The introduction of bulk-fill composites capable of being cured within 3 s is attractive from a clinical standpoint, not only for its time-savings and cost-effectiveness [11,12] but also because a simpler procedure diminishes the risk of iatrogenic errors [13]. The idea of using a short curing time in conjunction with a high light intensity is not new, as it has previously been proposed for plasma-arc curing units [14]. However, these curing units were poorly accepted by dental practitioners due to their high cost and inconvenient handling. High-intensity light-curing became a more viable option due to recent advancements in LED technology, which enabled the construction of lightweight battery-powered devices, which emit intense light in a precisely defined wavelength range [15].

As a means of controlling polymerization shrinkage stress, various compositional modifications have been employed in bulk-fill composites, including the use of resin systems with high molecular weight monomers [16], fillers with low elastic modulus [17], and additives for modification of the polymerization reaction [18]. These strategies have proven successful for maintaining shrinkage properties of bulk-fill composites at levels that are similar or lower than those produced by conventional composites [13]. However, polymerization shrinkage kinetics of bulk-fill composites cured with high-intensity LED units (above 3000 mW/cm^2) has not been investigated thus far.

Therefore, the aim of this study was to compare the effect of a high-intensity and a conventional curing protocol on shrinkage properties of conventional and bulk-fill composites, including two bulk-fill composites specifically designed for high-intensity (sometimes regarded as "ultra-fast" [10,19]) light-curing. The first null hypothesis assumed no effect of the curing protocol on the following properties: (1) linear polymerization shrinkage, (2) degree of conversion (DC), (3) shrinkage force, (4) maximum shrinkage force rate, and (5) time to achieve maximum shrinkage force rate. The second null hypothesis assumed no differences among composite materials regarding the aforementioned properties.

2. Materials and methods

2.1. Composite materials and light-curing protocols

Seven resin composites were investigated in order to include materials representative for different material classes, i.e. conventional, bulk-fill, sculptable, and flowable composites (Table 1). Two of the investigated materials (Tetric PowerFill and Tetric PowerFlow) are specifically designed for high-intensity light-curing.

For all measurements, light-curing was performed using a violet-blue LED curing unit (Bluephase PowerCure, Ivoclar Vivadent, Schaan, Liechtenstein; emission wavelength range: 390–500 nm). Two curing protocols were investigated: the protocol designated as "3-s" involved light-curing for 3 s with a radiant exitance of 3440 mW/cm^2 (radiant exposure = 10.3 J/cm^2), whereas the protocol designated as "conventional" involved light-curing for 10 s with a radiant exitance of 1340 mW/cm^2 (radiant exposure = 13.4 J/cm^2). The radiant exitance values were measured and periodically verified using a calibrated and NIST-referenced UV–vis spectrophotometer system (MARC; BlueLight Analytics, Halifax, Canada).

2.2. Linear shrinkage

Real-time linear shrinkage measurements were performed using a custom-made linometer, as described previously [20–23]. Briefly, the device consisted of a solid metal frame on which a thin aluminum platelet was loosely placed. From the bottom side of the platelet, a perpendicular diaphragm extended into a recess of the linometer's infrared measuring sensor. A standardized amount of composite material (42 mm^3) was placed on the upper side of the platelet and flattened using a glass plate to obtain a 1.5 mm thick discoid composite specimen. The light guide tip of the curing unit (PowerCure, Ivoclar Vivadent) was positioned in direct contact with the glass plate, and the composite specimen was light-cured through the glass plate according to the protocols described above. The vertical movement of the diaphragm due to polymerization shrinkage was detected by the infrared sensor at a data

Table 1
Resin composites investigated in this study.

Composite viscosity	Composite type	Composite name (abbreviation)	Filler content (wt %/vol%)	Resin matrix	Photoinitiator	Manufacturer	shade / LOT No.
Flowable	Conventional	Tetric EvoFlow (TEF)	58/31	Bis-GMA, UDMA, decandioldimethacrylate	CQ/amine	Ivoclar Vivadent, Schaan, Liechtenstein	A2 / Y15650
	Bulk-fill	X-tra base (XB)	75/60	Bis-EMA, UDMA	CQ/amine	Voco, Cuxhaven, Germany,	universal / 1932130
		Tetric PowerFlow (PFW)	68/46	Bis-GMA, Bis-EMA, UDMA	CQ/amine + Ivocerin	Ivoclar Vivadent, Schaan, Liechtenstein	IVA / Y15023
Sculptable	Conventional	Ceram.x (CER)	76/57	Methacrylate modified polysiloxane, dimethacrylate resin	CQ/amine	Dentsply Sirona, Konstanz, Germany	A2 / 0189
	Bulk-fill	Filtek One Bulk Fill (FIL)	77/59	UDMA, aromatic UDMA, DDDMA, proprietary AFM	CQ/amine	3M Espe, St. Paul, MN, USA	A2 / NA60719
		Tetric EvoCeram Bulk Fill (TECBF)	77/54	Bis-GMA, Bis-EMA, UDMA	CQ/ amine + Ivocerin + Lucirin TPO	Ivoclar Vivadent, Schaan, Liechtenstein	IVA / Y16932
		Tetric PowerFill (PFL)	77/54	Bis-GMA, Bis-EMA, UDMA, propoxylated bisphenol A dimethacrylate, DCP	CQ/ amine + Ivocerin + Lucirin TPO	Ivoclar Vivadent, Schaan, Liechtenstein	IVA / X56571

The information on material composition was provided by respective manufacturers.
Bis-GMA: Bisphenol-A-glycidyldimethacrylate, Bis-EMA: ethoxylated bisphenol-A-dimethacrylate, TEGDMA triethylene glycol dimethacrylate, UDMA: urethane dimethacrylate, DCP: tricyclodecane-dimethanol dimethacrylate, DDDMA: 1, 12-dodecanediol dimethacrylate, AFM: addition fragmentation monomer, CQ: camphorquinone, TPO: 2,4,6-trimethylbenzoyldiphenylphosphine oxide.

collection rate of 5 Hz and an accuracy of 0.1 μm. Real-time measurements were performed for 15 min from the start of light-curing, inside a temperature-controlled chamber at 25 ± 1 °C, which simulated intraoral temperature after rubber-dam isolation [24]. The linear shrinkage data were logged by a personal computer, using an analog-to-digital converter and custom-made software. Eight repetitions were performed for each experimental group (n = 8).

2.3. Degree of conversion

After completing the linear shrinkage measurements (15 min post irradiation), specimens were removed from the linometer and mounted onto a diamond attenuated total reflectance (ATR) accessory of a Fourier transform infrared (FTIR) spectrometer (Cary 630 FTIR, Agilent Technologies, Santa Clara, CA, USA) to evaluate DC on the bottom side of 1.5 mm thick specimens. Therefore, the DC measurements were performed 15 min after the start of light-curing, according to a previously described procedure of evaluating the DC at the endpoint of the observation period for linear shrinkage and shrinkage force measurements [21,22].

The FTIR spectra were recorded with 100 scans, using a resolution of 4 cm^{-1} in the wavelength range of 400–4000 cm^{-1}. A background FTIR spectrum was collected before each measurement. Spectra from uncured composites were recorded under the same conditions. Eight repetitions were performed for each experimental group (n = 8). DC was calculated from the changes in the ratio of absorbance intensities (peak heights) of aliphatic C═C (1638 cm^{-1}) and aromatic C···C (1608 cm^{-1}) spectral bands using the following equation [25]:

$$DC\ (\%) = \left(1 - \frac{(1638\ cm^{-1} / 1608\ cm^{-1})\ \text{after curing}}{(1638\ cm^{-1} / 1608\ cm^{-1})\ \text{before curing}}\right) \times 100$$

2.4. Shrinkage force

Real-time measurements of shrinkage force were performed using a custom-made stress analyzer, as described in previous studies [20–22]. The semi-rigid setup featured compliance of 0.4 μm/N in order to approximate a clinically realistic situation in which shrinkage force is partially relieved by the displacement of dental hard tissues [26]. Briefly, a load cell (PM 11-K; Mettler, Greifensee, Switzerland) was connected to a metal cylinder, on which a standardized amount (42 mm^3) of the composite material was placed and flattened to a thickness of 1.5 mm by a glass plate. This procedure produced discoid composite specimens with the base surface area of 28 mm^2. As both bases of the discoid specimens were bonded, the ratio of bonded to unbonded surface area (C-factor) was 2.0. The glass plate and metal cylinder were prepared by sandblasting with aluminum oxide (50 μm; Renfert, Hilzingen, Germany), rinsing with a stream of demineralized water for 30 s, drying using pressurized air stream, and applying a thin layer of Monobond Plus (Ivoclar Vivadent). Subsequently, the glass plate and metal cylinder were inspected using a stereomicroscope at 40× magnification (M3Z; Leica/Wild, Heerbrugg, Switzerland) to confirm that no aluminum oxide particles remained on the sandblasted surfaces. Light-curing of the composite specimen was performed through the glass plate, according to the above described protocols. Forces generated by polymerization shrinkage were detected by the load cell at a data collection rate of 5 Hz and accuracy of 0.001 N. Real-time measurements were performed for 15 min from the start of light-curing, inside a temperature-controlled chamber at 25 ± 1 °C. The shrinkage force data were logged by a personal computer, using an analog-to-digital converter and custom-made software. Eight repetitions were performed for each experimental group (n = 8). The obtained polymerization shrinkage force curves were plotted as a function of time, and first derivatives of these curves were calculated to represent the shrinkage force rate. Plotting the first derivatives vs. time enabled the extraction of kinetic parameters: maximum shrinkage force rate and time to achieve maximum shrinkage force rate.

2.5. Statistical analysis

Normality of distribution and homogeneity of variances were checked using Levene's and Shapiro-Wilk's tests, respectively. Mean values of linear shrinkage, DC, shrinkage force, maximum shrinkage force rate and time to achieve maximum shrinkage force rate were compared among the combinations of composites and curing protocols using one-way ANOVA with Tukey's post-hoc adjustment. The relationship between linear shrinkage and shrinkage force was investigated using Pearson's correlation analysis. The statistical analysis was performed using SPSS (version 20, IBM, Armonk, NY, USA) at an overall level of significance of α = 0.05.

3. Results

Figs. 1 and 2 show the development of linear shrinkage and shrinkage force as a function of time, respectively. The curves in Fig. 1 were used to determine the linear shrinkage values at the end of the 15-min observation period, whereas the curves in Fig. 2 were used to determine the shrinkage force at the end of the 15-min observation period, and the related kinetic parameters: maximum shrinkage rate and time to achieve maximum shrinkage force rate.

Fig. 3 shows linear shrinkage values measured 15 min after the start of light-curing. Linear shrinkage of flowable composites (1.93–2.91 %) was significantly higher compared to that of sculptable composites (1.15–1.54 %). In comparison to the conventional curing, the 3-s curing led to significantly lower linear shrinkage values for flowable composites (TEF, PFW, and XB). In contrast, linear shrinkage of the sculptable composites was unaffected by the curing protocol.

The DC values measured 15 min after the start of light-curing were in the range of 45.8–60.1 % (Fig. 4). Compared to the conventional curing, the 3-s curing led to significantly lower DC values for the materials TEF, FIL, and XB. The DC of the other materials was unaffected by the curing protocol.

Fig. 5 shows shrinkage force values measured 15 min after the start of light-curing. Flowable composites generated significantly higher shrinkage forces (18.7–24.4 N) than all sculptable composites (13.5–17.0 N) except CER. For CER, the shrinkage force measured using the conventional curing (17.3 N) was statistically similar to the lowest shrinkage force value measured within the group of flowable composites (18.7 N, for XB cured with the 3-s protocol). Compared to the conventional curing, the 3-s curing led to significantly lower shrinkage forces for the flowable bulk-fill composites PFW and XB. In contrast, FIL showed a significantly higher shrinkage force for the 3-s curing. Shrinkage forces of the other composites remained unaffected by the curing protocol.

Maximum shrinkage force rates ranged between 1.13–3.40 N/s (Fig. 6). For CER, TEF, PFL, PFW, and FIL significantly higher values of maximum shrinkage force rate were identified for the 3-s curing compared to the conventional curing. In contrast, for TECBF and XB, the curing protocol showed no significant effect on maximum shrinkage force rate.

The time to achieve maximum shrinkage force rate ranged between 0.89–5.06 s (Fig. 7). For TEF, PFL, PFW, FIL, and XB, significantly shorter times were identified when the 3-s curing was used instead of the conventional curing. For CER and TECBF, the curing protocol had no significant effect on the time to achieve maximum shrinkage force rate.

In Fig. 8, the shrinkage force measured after 15 min was plotted as a function of linear shrinkage measured after the same time period. Highly significant positive correlations between these two parameters were identified with correlation coefficients of 0.91–0.93.

4. Discussion

This study investigated the effect of a high-intensity ("3-s") and a conventional curing protocol on shrinkage properties of bulk-fill and

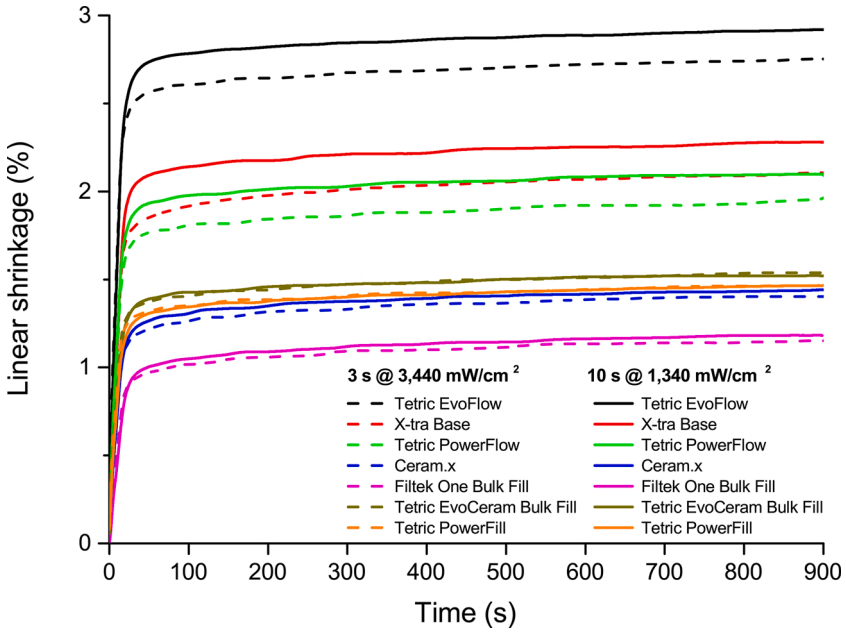

Fig. 1. Averaged curves of linear shrinkage. Dashed lines denote high-intensity light-curing, while continuous lines denote conventional light-curing.

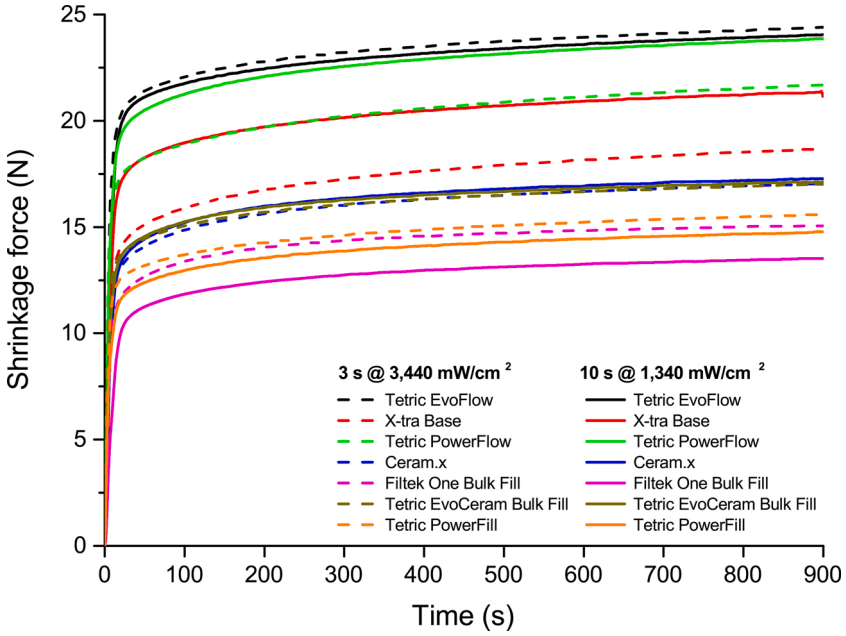

Fig. 2. Averaged curves of shrinkage force. Dashed lines denote high-intensity light-curing, while continuous lines denote conventional light-curing.

conventional composites. As the evaluated properties (linear shrinkage, DC, shrinkage force, maximum shrinkage force rate, and time to achieve maximum shrinkage force rate) were affected by the curing protocol for some of the investigated composites, the first null hypothesis was rejected. The second null hypothesis was rejected because the evaluated properties differed among the investigated composites. The shrinkage properties of two bulk-fill composites specifically designed for high-intensity light-curing were within the range of the other investigated materials.

The evaluation of linear shrinkage was complemented by DC measurements performed at the end of the 15-min observation period, as unconstrained shrinkage is known to correlate with the extent of polymerization [27]. Therefore, significantly lower linear shrinkage values measured for TEF and XB cured with the 3-s protocol compared to the conventional protocol can be attributed to the corresponding significantly lower DC attained by using the 3-s curing. For PFW, significantly lower linear shrinkage was measured for the 3-s curing compared to the conventional curing, but the corresponding DC difference was insufficient to produce a statistically significant result. An inverse outcome was observed for FIL, which reached significantly lower DC for the 3-s curing compared to the conventional curing; however, the corresponding difference in linear shrinkage values was insufficient to produce statistical significance. Given that the overall observed statistical power for detecting differences among materials and curing protocols for the linear shrinkage and DC data was > 0.999 at $\alpha = 0.05$, the lack of statistical significance in the aforementioned cases indicates that these small differences were negligible when considered in the context of much more pronounced inter-material differences.

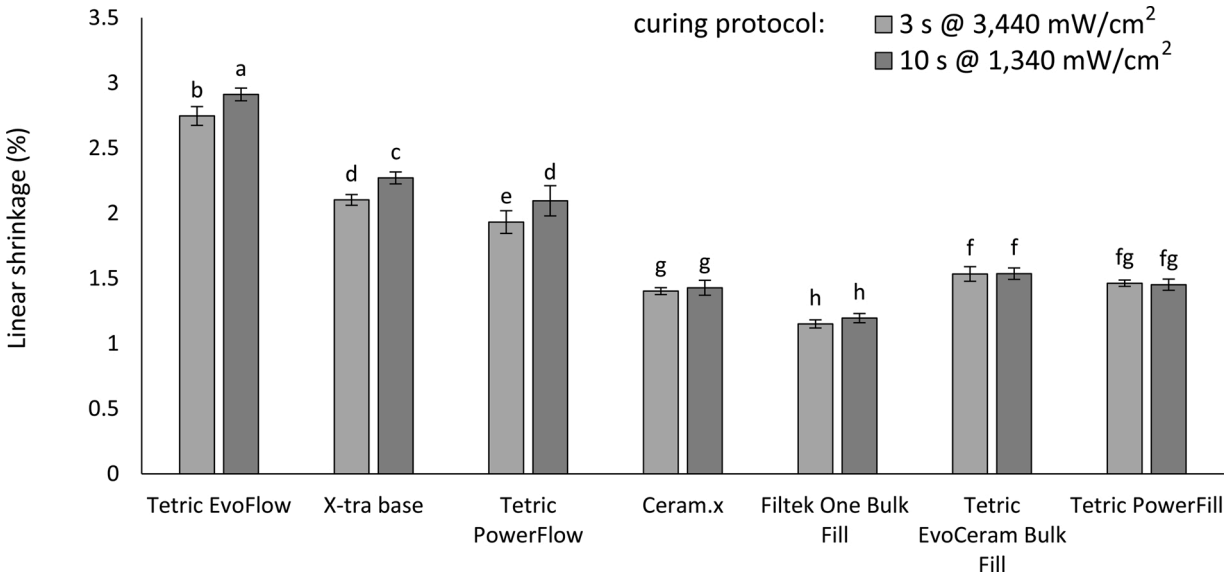

Fig. 3. Linear shrinkage (mean values ± standard deviation) measured after 15 min. Same letters denote statistically homogeneous groups.

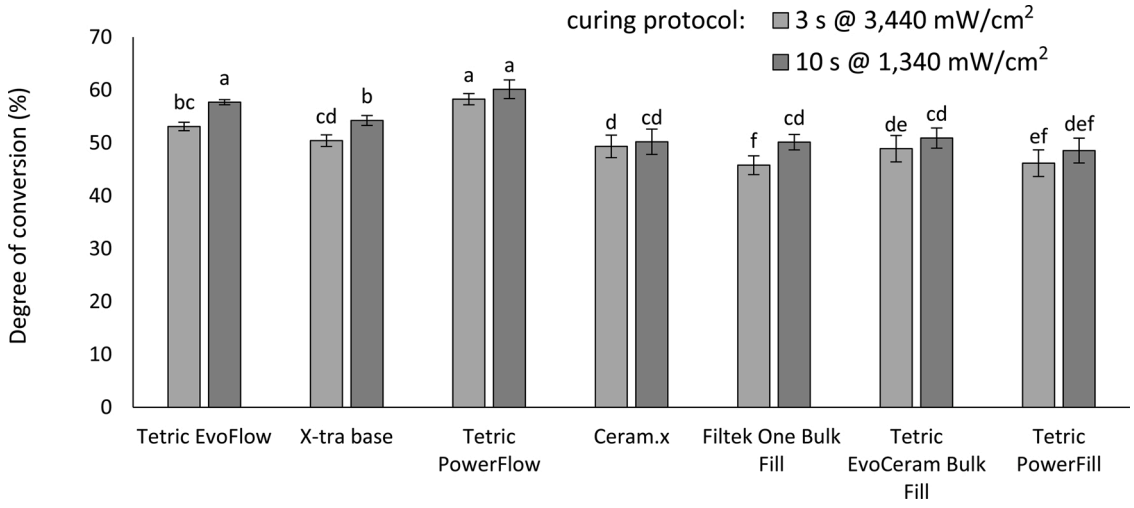

Fig. 4. Degree of conversion (mean values ± standard deviation) measured after 15 min. Same letters denote statistically homogeneous groups.

While DC was unaffected by the curing protocol in four out of seven materials, significantly lower DC values for the 3-s curing were identified for two flowable composites (TEF and XB) and FIL. These results can be attributed to a lower radiant exposure produced by the 3-s curing compared to the conventional curing, but also to a higher sensitivity of the aforementioned composites to bimolecular termination. The mobility of reactive species during polymerization has been recognized as a determining factor for the effect of high-intensity light-curing on the frequency of bimolecular termination [28]. Due to this effect, flowable composites are generally more prone to bimolecular termination and thus premature loss of free radicals caused by high-intensity light-curing [14,29]; the same rationale can be applied to explain the DC results for the flowable composites TEF and XB in this study. Considering a similar finding of a lower DC due to the 3-s curing identified in FIL, it can be speculated that its proprietary resin system capable of addition-fragmentation chain transfer (AFCT) [30] allowed better mobility of reactive species and consequently a higher rate of bimolecular termination. This mechanism may have caused the sculptable composite FIL to respond to high-intensity curing in a manner that is more commonly observed in flowable composites [14].

The relationship between linear shrinkage and shrinkage force depends on the construction of the measuring device due to the effect of dynamic changes in composite's elastic modulus on the development of shrinkage force [31]. In low-compliance devices, which use a feedback system for compensating the displacement, shrinkage force is primarily influenced by the composite's elastic modulus [32]. Using this type of device bears a risk of overestimating shrinkage forces due to neglecting the inherent compliance of tooth cavity walls [33]. In contrast, when devices of higher compliance are used, the most influential factor for the development of shrinkage force is the amount of linear shrinkage [34]. This was the case in the present study, in which a semi-rigid device was used, and consequently a high correlation of shrinkage force with linear shrinkage was observed. In Pearson correlation plots, flowable composites occupied the high-end of linear shrinkage and shrinkage force values, whereas the sculptable composites settled at the low-end, indicating that the obtained correlation can also be interpreted considering the differences in composite's filler load [21]. However, a quantitative analysis of this aspect was not performed due to the fact that four out of seven composites (PFL, PFL, TECBF, TEF) contained pre-polymerized fillers, which are not directly comparable regarding mechanical

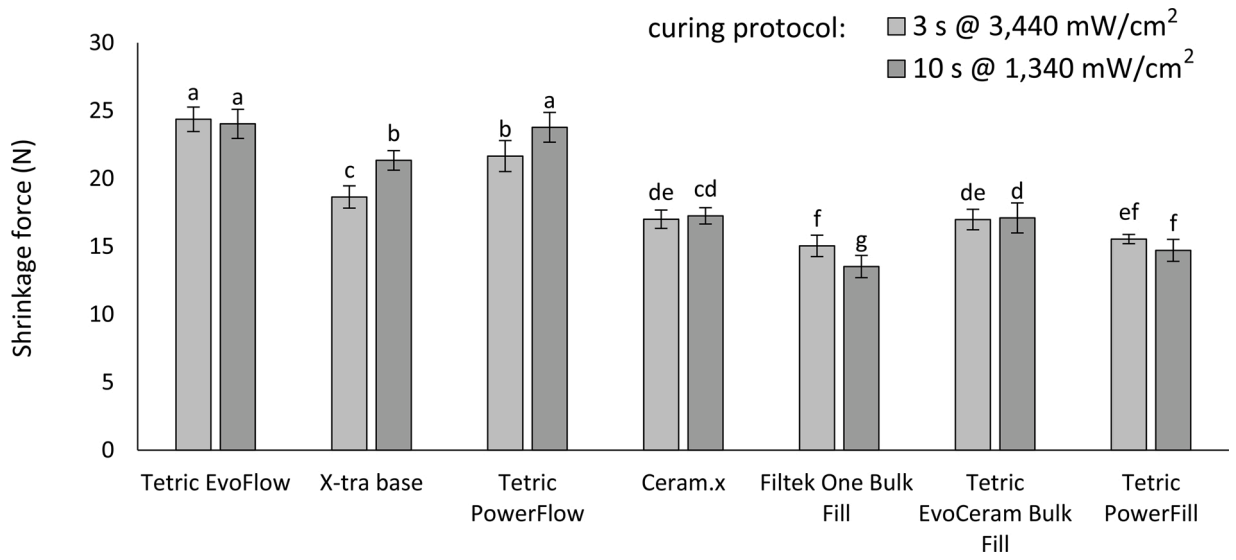

Fig. 5. Shrinkage force (mean values ± standard deviation) measured after 15 min. Same letters denote statistically homogeneous groups.

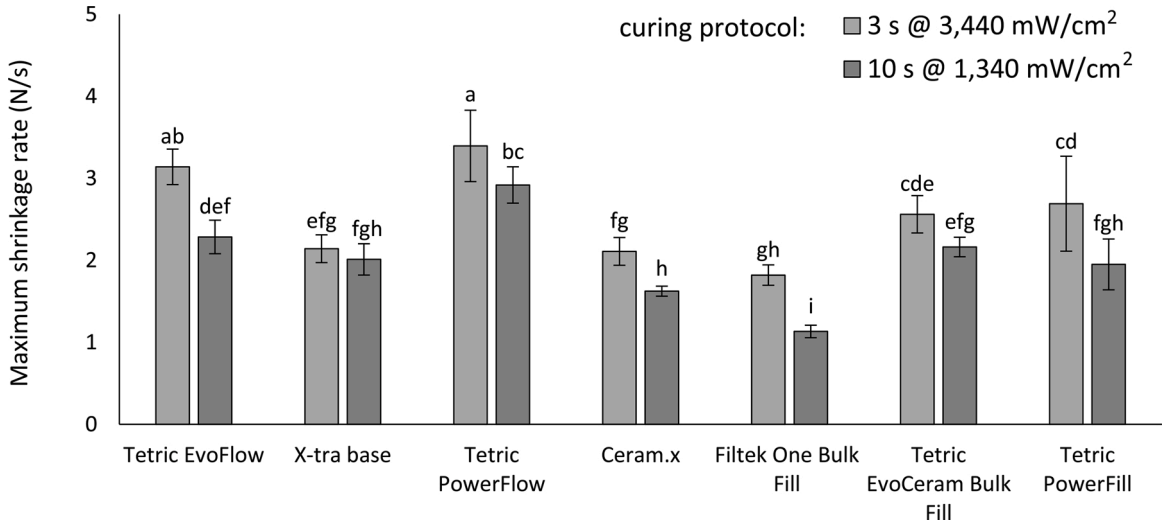

Fig. 6. Maximum shrinkage force rate (mean values ± standard deviation). Same letters denote statistically homogeneous groups.

properties to purely inorganic fillers [35].

A study of model composites based on a resin system comprising bisphenol-A glycidyl methacrylate and triethyleneglycol dimethacrylate has demonstrated how variations in radiant exitances (400–3000 mW/cm^2) can exert a twofold effect on shrinkage stress, depending on material composition [36]. According to that study, increasing radiant exitance while maintaining a constant radiant exposure can either decrease or increase polymerization shrinkage stress. If the composite's viscosity allows high mobility of reactive species during polymerization, its DC is diminished by a higher frequency of bimolecular termination, which in turn decreases shrinkage stress. On the other hand, in high-viscosity composites that are less sensitive to bimolecular termination, increased radiant exitance can improve DC, thereby increasing polymerization shrinkage [36]. The potential of high-intensity light-curing to affect shrinkage stress in both directions was also demonstrated in the present study; by increasing the radiant exitance, shrinkage force was either decreased (in PFW and XB), increased (in FIL), or left unaffected (in CER, TEF, TECBF, and PFL). The significantly lower shrinkage force resulting from the 3-s curing compared to the conventional curing for composites PFW and XB corresponds to significantly lower linear shrinkage values for the 3-s curing, which is in agreement with linear shrinkage being the main determinant of shrinkage force in the semi-rigid experimental setup used in this study [34]. An unexpected result was obtained for FIL, which showed significantly higher shrinkage force for the 3-s curing compared to the conventional curing, despite showing no significant effect of the curing protocol on linear shrinkage, and even presenting significantly lower DC values for the 3-s curing. Due to the lack of detailed compositional information for FIL, it is only possible to speculate that proprietary AFCT chemistry was more efficient in relieving the development of shrinkage force when the conventional curing protocol was used.

Kinetic parameters derived from real-time shrinkage force curves (maximum shrinkage force rate and time to achieve maximum shrinkage force rate) were highly sensitive for characterizing the initial stage of polymerization [32], thereby providing better discriminative power than absolute values of polymerization shrinkage and shrinkage force recorded after 15 min. Compared to the conventional curing, the 3-s curing resulted in 6–61 % higher maximum shrinkage force rates, and 15–53 % shorter times to achieve maximum shrinkage force rates. Much smaller relative differences between curing protocols were identified for

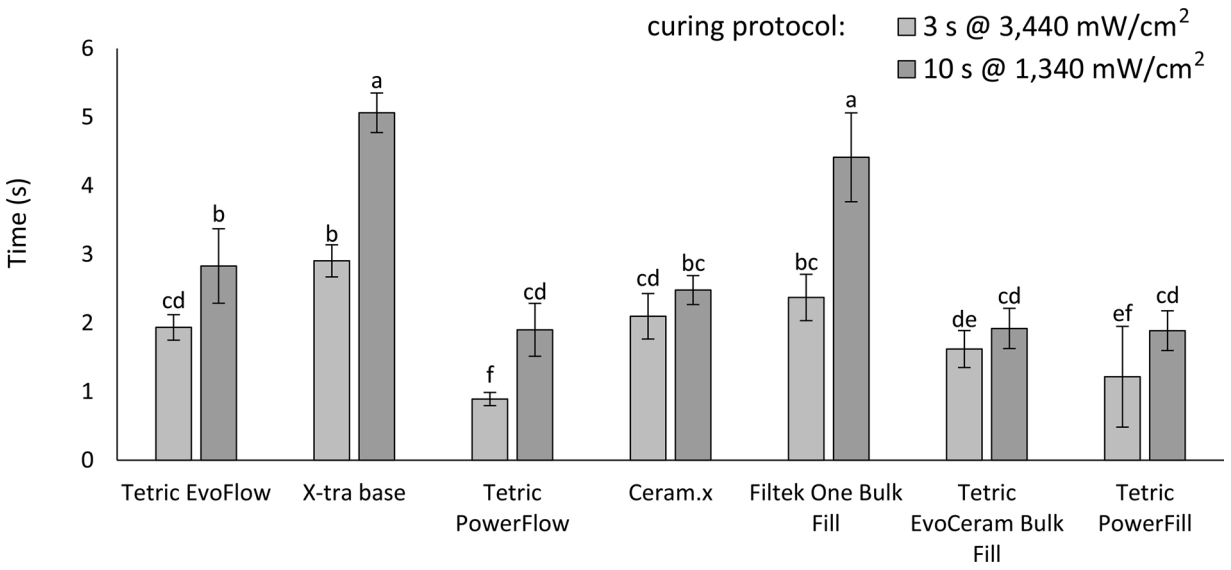

Fig. 7. Time to achieve maximum shrinkage force rate (mean values ± standard deviation). Same letters denote statistically homogeneous groups.

linear shrinkage and shrinkage force after 15 min (below 8 % and 13 %, respectively). Therefore, kinetic parameters yielded a larger effect size and more statistically significant results for comparisons between curing protocols; for five out of seven composites, including the composites specifically designed for fast curing, the maximum shrinkage force rates were significantly higher and the times to achieve maximum shrinkage force rates were significantly shorter for the 3-s curing compared to the conventional curing. The fact that the early stage of polymerization tends to be significantly affected by high-intensity curing indicates the need for assessing possible consequences of fast polymerization on restoration's marginal integrity. A future investigation on this topic is planned as a sequel to the present study.

Most parameters used for describing the shrinkage behavior (linear shrinkage, shrinkage force, and maximum shrinkage force rate) of two bulk-fill composites specifically designed for high-intensity curing were within the range of values measured for other composites belonging to the same viscosity group. Furthermore, the effect of high-intensity curing on linear shrinkage and shrinkage force after 15 min was similar to that identified for other materials of the corresponding viscosity, i.e. no significant effect of the curing protocol was observed for PFL, whereas significantly lower values for the 3-s curing were identified for PFW. The only parameter by which one of the materials specifically designed for high-intensity curing differed from other materials of the same viscosity was the time to achieve maximum shrinkage force rate, which was significantly shorter for PFW compared to the other flowable composites investigated. Additionally, the values of maximum shrinkage force rate and shrinkage force measured for PFW were among the highest of all investigated composites, indicating the need to further evaluate possible consequences of the fast and extensive development of shrinkage force on clinically relevant properties.

The bulk-fill composites designed for high-intensity curing (PFW and PFL) are compositionally similar to the previous line of composites from the same manufacturer. The manufacturer's information specifies that PFW features an identical composition as its predecessor (Tetric EvoFlow Bulk Fill, Ivoclar Vivadent), whereas PFL features a similar monomer, filler, and photoinitiator composition as its predecessor (TECBF), and additionally contains a β-allyl sulfone AFCT agent [37]. This compound decreases crosslinking density by favoring a more linear polymeric chain growth, thereby shifting the gel point to higher conversion values and ultimately reducing polymerization shrinkage stress [38]. To emphasize the reversibility of the reaction, this mechanism of controlling polymerization reaction has also been referred to as reversible addition-fragmentation chain transfer (RAFT) [10]. The approach of creating less crosslinked polymeric networks by employing AFCT/RAFT is not unique to PFL, as a similar approach is employed in FIL, in which the addition-fragmentation is attained through a specific functional group embedded within the proprietary methacrylate monomer [30]. The two materials employing the AFCT chemistry (PFL and FIL) demonstrated the lowest shrinkage forces among all materials investigated, which can be partly attributed to the benefit of gelation occurring at higher DC values.

This study showed that bulk-fill composites produced lower or similar shrinkage forces compared to conventional composites of the corresponding viscosity, which is in agreement with results from previous studies [34,39–44]. In the group of sculptable composites, shrinkage forces amounted to 13.5–17.1 N for bulk-fill composites vs. 17.0–17.3 N for the conventional composite; whereas in the group of flowable composites, shrinkage forces amounted to 18.7–23.8 N for bulk-fill composites vs. 24.0–24.4 N for the conventional composite. For other shrinkage parameters (linear shrinkage, maximum shrinkage rate, and time of maximum shrinkage rate), the distinction between the conventional and bulk-fill composites was less clear. As both the conventional and bulk-fill groups comprise compositionally heterogeneous materials, it is not surprising that differences in shrinkage properties among individual composites surpassed the differences between material classes.

All of the investigated composites contain the camphorquinone/amine photoinitiator system, whereas some of them additionally contain photoinitiators that react through a Norrish type I reaction, namely Ivocerin (composites TECBF, PFL, and PFW) and Lucirin TPO (composites TECBF and PFL) [10]. As Norrish type I photoinitiators were shown to be more effective for high-intensity curing than the traditional camphorquinone/amine photoinitiator system [36], it is interesting to note that all of the composites containing additional photoinitiators in this study reached statistically similar DC values regardless of curing protocols. On the other hand, all composites that contain exclusively camphorquinone/amine system (except CER) showed significantly lower DC values when cured with the 3-s protocol. Although the benefits of additional photoinitiators cannot be conclusively confirmed within the limitations of the present study, the obtained results nevertheless support their efficiency for high-intensity light-curing.

Linear shrinkage and shrinkage force were monitored for 15 min after the start of light-curing, according to previous studies which have shown that after 15 min these parameters reach about 90 % of their maximum

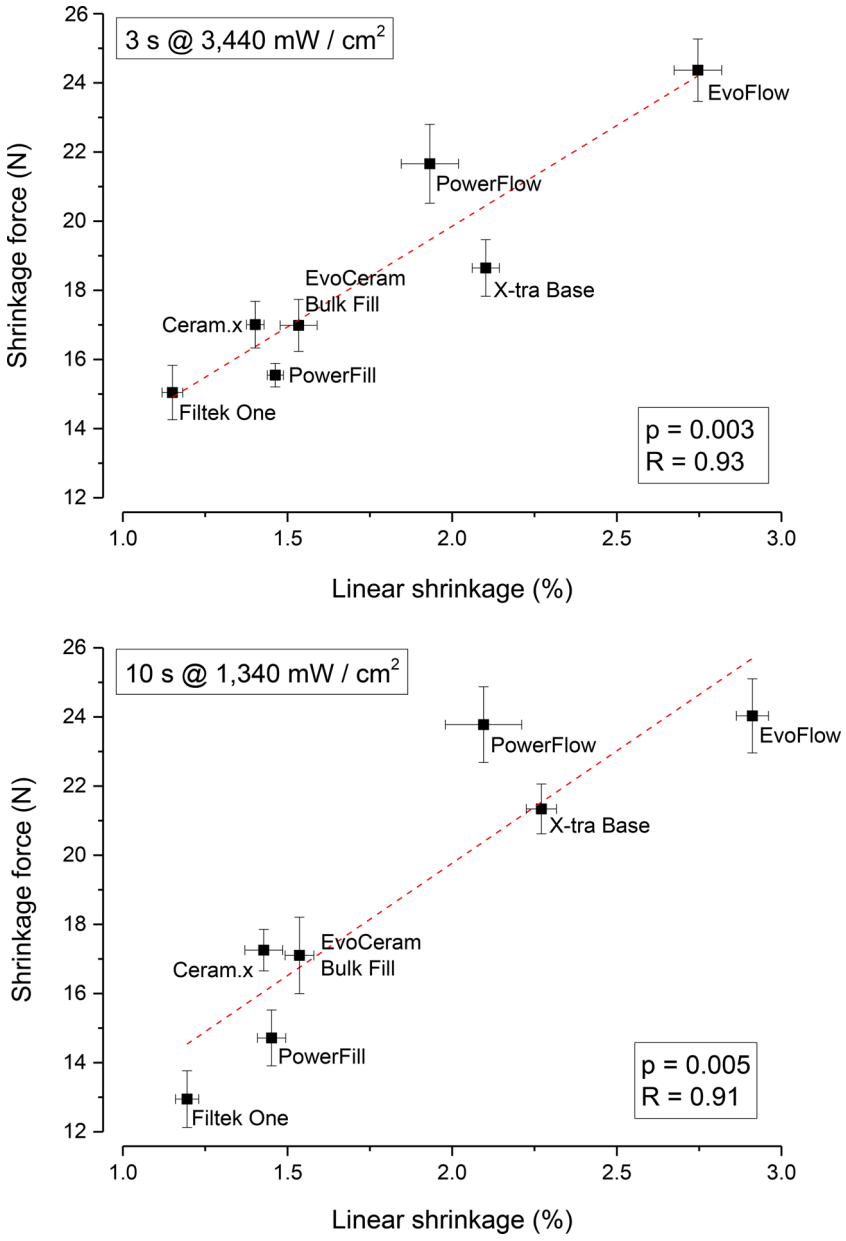

Fig. 8. Scatterplots of shrinkage force vs. linear shrinkage and results of Pearson correlation analysis. Error bars represent ± 1 standard deviation.

values measured after 24 h [5,22]. These studies have also shown that the slow development of linear shrinkage and shrinkage stress occurring after 15 min due to post-cure polymerization does not affect relative rankings of experimental groups. Therefore, capturing the ultimate values of linear shrinkage and shrinkage force [45] was not essential for relative comparisons among materials and curing protocols performed in this study.

In order to ensure sufficient penetration of curing light through all investigated composites, the measurements in this study were performed using 1.5 mm thick specimens. Whereas thicker layers appear more relevant for bulk-fill composites, increasing the thickness of discoid specimens to 4 mm in the current experimental setup would result in a C-factor of 0.75 and produce conditions conducive to stress relief [22]. Therefore, the layer thickness of 1.5 mm resulting in a C-factor of 2 was considered to provide optimally constrained conditions for a clinically relevant investigation of shrinkage force development [5,21,22].

Comparisons of different curing protocols are commonly performed by varying curing time and radiant exitance while maintaining constant radiant exposure [5,29,36]. Ensuring identical radiant exposures for curing protocols used in this study was technically not attainable because it would require precise control over the curing unit operation within very short time frames (< 1 s). Although not being identical, the radiant exposures produced by the 3-s and the conventional curing are comparable (10.3 and 13.4 J/cm^2, respectively) and reflect clinically realistic values used for curing with contemporary LED units [10,46].

5. Conclusions

Shrinkage behavior of 1.5 mm thick composite specimens under conditions of high-intensity light-curing was material-dependent. Despite a modest effect of high-intensity curing on static parameters (linear shrinkage and shrinkage force), the analysis of kinetic parameters revealed up to 61 % higher maximum shrinkage force rates, and up to 53 % shorter times to achieve maximum shrinkage force rates for high-intensity compared to conventional curing. Composites specifically designed for high-intensity curing demonstrated shrinkage properties

generally comparable to those of other investigated composites. Using additional photoinitiators and addition-fragmentation chain transfer agents appears beneficial for the reduction of shrinkage force and maintaining degree of conversion under conditions of high-intensity curing, respectively.

Funding

Matej Par's research stay at University of Zurich was funded by a grant of the Swiss Federal Department of Economic Affairs, Education and Research (2019.0221). This study was supported by the Croatian Science Foundation (Project IP-2019−04-6183, Biomimetic intelligent composite systems).

CRediT authorship contribution statement

Matej Par: Conceptualization, Investigation, Formal analysis, Visualization, Writing - original draft, Funding acquisition. **Danijela Marovic:** Conceptualization, Resources, Writing - review & editing, Funding acquisition. **Thomas Attin:** Conceptualization, Methodology, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition. **Zrinka Tarle:** Conceptualization, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition. **Tobias T. Tauböck:** Conceptualization, Methodology, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors report no declarations of interest.

Acknowledgment

The authors are grateful to the company Ivoclar Vivadent (Schaan, Liechtenstein) for donation of the curing unit and composite materials.

References

[1] J.L. Ferracane, Placing dental composites—a stressful experience, Oper. Dent. 33 (2008) 247–257, https://doi.org/10.2341/07-BL2.
[2] R.R. Braga, J.L. Ferracane, J.R. Condon, Polymerization contraction stress in dual-cure cements and its effect on interfacial integrity of bonded inlays, J. Dent. 30 (2002) 333–340, https://doi.org/10.1016/S0300-5712(02)00047-7.
[3] L.F.J. Schneider, L.M. Cavalcante, N. Silikas, Shrinkage stresses generated during resin-composite applications: a review, J. Dent. Biomech. 2010 (2010), 131630, https://doi.org/10.4061/2010/131630.
[4] J. Ferracane, Developing a more complete understanding of stresses produced in dental composites during polymerization, Dent. Mater. 21 (2005) 36–42, https://doi.org/10.1016/j.dental.2004.10.004.
[5] T.T. Tauböck, A.J. Feilzer, W. Buchalla, C.J. Kleverlaan, I. Krejci, T. Attin, Effect of modulated photo-activation on polymerization shrinkage behavior of dental restorative resin composites, Eur. J. Oral Sci. 122 (2014) 293–302, https://doi.org/10.1111/eos.12139.
[6] J. Stansbury, M. Trujillolemon, H. Lu, X. Ding, Y. Lin, J. Ge, Conversion-dependent shrinkage stress and strain in dental resins and composites, Dent. Mater. 21 (2005) 56–67, https://doi.org/10.1016/j.dental.2004.10.006.
[7] C. Charton, P. Colon, F. Pla, Shrinkage stress in light-cured composite resins: influence of material and photoactivation mode, Dent. Mater. 23 (2007) 911–920, https://doi.org/10.1016/j.dental.2006.06.034.
[8] M.M. Daugherty, W. Lien, M.R. Mansell, D.L. Risk, D.A. Savett, K.S. Vandewalle, Effect of high-intensity curing lights on the polymerization of bulk-fill composites, Dent. Mater. 34 (2018) 1531–1541, https://doi.org/10.1016/j.dental.2018.06.005.
[9] K.D. Jandt, R.W. Mills, A brief history of LED photopolymerization, Dent. Mater. 29 (2013) 605–617, https://doi.org/10.1016/j.dental.2013.02.003.
[10] N. Ilie, D.C. Watts, Outcomes of ultra-fast (3 s) photo-cure in a RAFT-modified resin-composite, Dent. Mater. 36 (2020) 570–579, https://doi.org/10.1016/j.dental.2020.02.007.
[11] M.D. Bellinaso, F.Z.M. Soares, R. de O. Rocha, Do bulk-fill resins decrease the restorative time in posterior teeth? A systematic review and meta-analysis of in vitro studies, J. Investig. Clin. Dent. 10 (2019), e12463, https://doi.org/10.1111/jicd.12463.
[12] T.T. Tauböck, D. Marovic, D. Zeljezic, A.D. Steingruber, T. Attin, Z. Tarle, Genotoxic potential of dental bulk-fill resin composites, Dent. Mater. 33 (2017) 788–795, https://doi.org/10.1016/j.dental.2017.04.011.
[13] A. Van Ende, J. De Munck, D.P. Lise, B. Van Meerbeek, Bulk-fill composites: a review of the current literature, J. Adhes. Dent. 19 (2017) 95–109, https://doi.org/10.3290/j.jad.a38141.
[14] D. Selig, T. Haenel, B. Hausnerová, B. Moeginger, D. Labrie, B. Sullivan, R.B. T. Price, Examining exposure reciprocity in a resin based composite using high irradiance levels and real-time degree of conversion values, Dent. Mater. 31 (2015) 583–593, https://doi.org/10.1016/j.dental.2015.02.010.
[15] J.E. Harlow, B. Sullivan, A.C. Shortall, D. Labrie, R.B. Price, Characterizing the output settings of dental curing lights, J. Dent. 44 (2016) 20–26, https://doi.org/10.1016/j.jdent.2015.10.019.
[16] N. Ilie, K. Stark, Effect of different curing protocols on the mechanical properties of low-viscosity bulk-fill composites, Clin. Oral Investig. 19 (2015) 271–279, https://doi.org/10.1007/s00784-014-1262-x.
[17] S. Bucuta, N. Ilie, Light transmittance and micro-mechanical properties of bulk fill vs. Conventional resin based composites, Clin. Oral Investig. 18 (2014) 1991–2000, https://doi.org/10.1007/s00784-013-1177-y.
[18] N. Ilie, J. Durner, Polymerization kinetic calculations in dental composites: a method comparison analysis, Clin. Oral Investig. 18 (2014) 1587–1596, https://doi.org/10.1007/s00784-013-1128-7.
[19] L.D. Randolph, W.M. Palin, S. Bebelman, J. Devaux, B. Gallez, G. Leloup, J. G. Leprince, Ultra-fast light-curing resin composite with increased conversion and reduced monomer elution, Dent. Mater. 30 (2014) 594–604, https://doi.org/10.1016/j.dental.2014.02.023.
[20] M.M. Stavridakis, D. Dietschi, I. Krejci, Polymerization shrinkage of flowable resin-based restorative materials, Oper. Dent. 30 (2005) 118–128.
[21] T.T. Tauböck, F. Jäger, T. Attin, Polymerization shrinkage and shrinkage force kinetics of high- and low-viscosity dimethacrylate- and ormocer-based bulk-fill resin composites, Odontology 107 (2019) 103–110, https://doi.org/10.1007/s10266-018-0369-y.
[22] T.T. Tauböck, Z. Tarle, D. Marovic, T. Attin, Pre-heating of high-viscosity bulk-fill resin composites: effects on shrinkage force and monomer conversion, J. Dent. 43 (2015) 1358–1364, https://doi.org/10.1016/j.jdent.2015.07.014.
[23] S. Lottanti, T.T. Tauböck, M. Zehnder, Shrinkage of backfill gutta-percha upon cooling, J. Endod. 40 (2014) 721–724, https://doi.org/10.1016/j.joen.2013.09.043.
[24] P.J.M.M. Plasmans, N.H.J. Creugers, R.J. Hermsen, M.M.A. Vrijhoef, Intraoral humidity during operative procedures, J. Dent. 22 (1994) 89–91, https://doi.org/10.1016/0300-5712(94)90007-8.
[25] M. Par, N. Spanovic, T.T. Tauböck, T. Attin, Z. Tarle, Degree of conversion of experimental resin composites containing bioactive glass 45S5: the effect of post-cure heating, Sci. Rep. 9 (2019) 17245, https://doi.org/10.1038/s41598-019-54035-y.
[26] T.T. Tauböck, T. Bortolotto, W. Buchalla, T. Attin, I. Krejci, Influence of light-curing protocols on polymerization shrinkage and shrinkage force of a dual-cured core build-up resin composite: shrinkage and force of dual-cured composite, Eur. J. Oral Sci. 118 (2010) 423–429, https://doi.org/10.1111/j.1600-0722.2010.00746.x.
[27] M. Dewaele, D. Truffier-Boutry, J. Devaux, G. Leloup, Volume contraction in photocured dental resins: the shrinkage-conversion relationship revisited, Dent. Mater. 22 (2006) 359–365, https://doi.org/10.1016/j.dental.2005.03.014.
[28] S.V. Palagummi, T. Hong, Z. Wang, C.K. Moon, M.Y.M. Chiang, Resin viscosity determines the condition for a valid exposure reciprocity law in dental composites, Dent. Mater. 36 (2020) 310–319, https://doi.org/10.1016/j.dental.2019.12.003.
[29] M. Hadis, J.G. Leprince, A.C. Shortall, J. Devaux, G. Leloup, W.M. Palin, High irradiance curing and anomalies of exposure reciprocity law in resin-based materials, J. Dent. 39 (2011) 549–557, https://doi.org/10.1016/j.jdent.2011.05.007.
[30] N. Ilie, Sufficiency of curing in high-viscosity bulk-fill resin composites with enhanced opacity, Clin. Oral Investig. 23 (2019) 747–755, https://doi.org/10.1007/s00784-018-2482-2.
[31] J.B.C. Meira, R.R. Braga, R.Y. Ballester, C.B. Tanaka, A. Versluis, Understanding contradictory data in contraction stress tests, J. Dent. Res. 90 (2011) 365–370, https://doi.org/10.1177/0022034510388039.
[32] Z. Wang, M.Y.M. Chiang, System compliance dictates the effect of composite filler content on polymerization shrinkage stress, Dent. Mater. 32 (2016) 551–560, https://doi.org/10.1016/j.dental.2016.01.006.
[33] G.A. Laughlin, J.L. Williams, J.D. Eick, The influence of system compliance and sample geometry on composite polymerization shrinkage stress, J. Biomed. Mater. Res. 63 (2002) 671–678, https://doi.org/10.1002/jbm.10386.
[34] H. Al Sunbul, N. Silikas, D.C. Watts, Polymerization shrinkage kinetics and shrinkage-stress in dental resin-composites, Dent. Mater. 32 (2016) 998–1006, https://doi.org/10.1016/j.dental.2016.05.006.
[35] L.D. Randolph, W.M. Palin, G. Leloup, J.G. Leprince, Filler characteristics of modern dental resin composites and their influence on physico-mechanical properties, Dent. Mater. 32 (2016) 1586–1599, https://doi.org/10.1016/j.dental.2016.09.034.
[36] W.M. Palin, M.A. Hadis, J.G. Leprince, G. Leloup, L. Boland, G.J.P. Fleming, G. Krastl, D.C. Watts, Reduced polymerization stress of MAPO-containing resin composites with increased curing speed, degree of conversion and mechanical properties, Dent. Mater. 30 (2014) 507–516, https://doi.org/10.1016/j.dental.2014.02.003.
[37] C. Gorsche, M. Griesser, G. Gescheidt, N. Moszner, R. Liska, β-allyl sulfones as addition–fragmentation chain transfer reagents: a tool for adjusting thermal and

mechanical properties of dimethacrylate networks, Macromolecules. 47 (2014) 7327–7336, https://doi.org/10.1021/ma501550b.
[38] C. Gorsche, T. Koch, N. Moszner, R. Liska, Exploring the benefits of β-allyl sulfones for more homogeneous dimethacrylate photopolymer networks, Polym. Chem. 6 (2015) 2038–2047, https://doi.org/10.1039/C4PY01582G.
[39] H. El-Damanhoury, J. Platt, Polymerization shrinkage stress kinetics and related properties of bulk-fill resin composites, Oper. Dent. 39 (2014) 374–382, https://doi.org/10.2341/13-017-L.
[40] R.J.-Y. Kim, Y.-J. Kim, N.-S. Choi, I.-B. Lee, Polymerization shrinkage, modulus, and shrinkage stress related to tooth-restoration interfacial debonding in bulk-fill composites, J. Dent. 43 (2015) 430–439, https://doi.org/10.1016/j.jdent.2015.02.002.
[41] C.M.P. Rosatto, A.A. Bicalho, C. Veríssimo, G.F. Bragança, M.P. Rodrigues, D. Tantbirojn, A. Versluis, C.J. Soares, Mechanical properties, shrinkage stress, cuspal strain and fracture resistance of molars restored with bulk-fill composites and incremental filling technique, J. Dent. 43 (2015) 1519–1528, https://doi.org/10.1016/j.jdent.2015.09.007.
[42] J.-H. Jang, S.-H. Park, I.-N. Hwang, Polymerization shrinkage and depth of cure of bulk-fill resin composites and highly filled flowable resin, Oper. Dent. 40 (2015) 172–180, https://doi.org/10.2341/13-307-L.
[43] J. Zorzin, E. Maier, S. Harre, T. Fey, R. Belli, U. Lohbauer, A. Petschelt, M. Taschner, Bulk-fill resin composites: polymerization properties and extended light curing, Dent. Mater. 31 (2015) 293–301, https://doi.org/10.1016/j.dental.2014.12.010.
[44] D. Marovic, T.T. Tauböck, T. Attin, V. Panduric, Z. Tarle, Monomer conversion and shrinkage force kinetics of low-viscosity bulk-fill resin composites, Acta Odontol. Scand. 73 (2015) 474–480, https://doi.org/10.3109/00016357.2014.992810.
[45] W. Germscheid, L.G. de Gorre, B. Sullivan, C. O'Neill, R.B. Price, D. Labrie, Post-curing in dental resin-based composites, Dent. Mater. 34 (2018) 1367–1377, https://doi.org/10.1016/j.dental.2018.06.021.
[46] V. Miletic, P. Pongprueksa, J. De Munck, N.R. Brooks, B. Van Meerbeek, Curing characteristics of flowable and sculptable bulk-fill composites, Clin. Oral Investig. 21 (2017) 1201–1212, https://doi.org/10.1007/s00784-016-1894-0.